Nuclear Magnetic Resonance F61/F62

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Prerequisites:

The knowledge of the following physics/math concepts is required for F61/F62:

- Classical mechanics: angular momentum, torque

- Electrodynamics: Magnetic dipole, magnetization, interaction magnetic dipole with magnetic field, precession, Larmor frequency, Helmholtz coils, Lenz's rule, Biot-Savart law

- Thermodynamics: Fermi-Dirac statistic, Boltzmann statistic

- Quantum mechanics: Perturbation theory

- Mathematics: discrete Fourier transformation, Nyquist frequency, Parseval's theorem

The physics lab experiment F61/F62 is organized into three parts. The measurements of the first two parts are carried out with a Bruker minispec p20 apparatus whereas the third part is measured with a newer Bruker minispec mq7.5 model. The experimental program of F61 and F62 is identical. Due to the organization of this lab experiment into three parts with two Nuclear Magnetic Resonance analyzers, F61 starts monday whereas the starting day of F62 is wednesday.

The three parts of this experiment are the following:

- Measurement of relaxation times

  The spin-lattice relaxation time T_1 and the spin-spin relaxation time T_2 are measured. The spin-spin relaxation time is measured by the spin echo as well as by the Carr-Purcell method.

- Measurement of chemical shift

  The chemical shift of protons is measured and used to identify five different substances.

- Imaging measurements in one and two dimensions

  Nuclear Magnetic Resonance techniques are used for imaging measurements in one and two dimensions. The flow of oil in sand is measured as a time dependent process in one dimension. Two dimensional measurements are carried out to map the inner volume of substances which contain oil or water.

Printer utilities

Two printers located in the same room are available for printing:

- F61: - Black and white printer

- F61-color: - Color printer

Inhaltsverzeichnis

Abbildungsverzeichnis

Data display

The LabVIEW programs display the data on graphic panels. You can save the display of a panel in encapsulated postscript format (.eps) in the following way:

- right click on the panel which you want to save, move cursor to *"Export"*, left click *"Export Simplified Image"*.

- A GUI *"Export Simplified Image"* will open. In this GUI, left click "Encapsulated Postscript (.eps)", then left click on the folder symbol next to the empty string field.

- A GUS "Save Image as" will open. In this GUI, define the folder in the top string field, then enter the file name in the string field "Dateiname" at the bottom. Left click "OK".

- Back in the GUI "Export Simplified Image", left click *"Save"*, the file now exists in the specified folder. You can view the contents of the file with XnView by double left click on the file name.

1   Basics of Nuclear Magnetic Resonance

Nuclear Magnetic Resonance (NMR) techniques are based on the fact that nuclei with spin S unequal zero possess a magnetic dipole moment,

$$\vec{\mu} = \hbar\gamma\vec{S}. \tag{1}$$

The quantity γ is called the gyromagnetic ratio of the nucleus. In the following, we restrict the discussion to the case of protons for which

$$\gamma_{Proton} = 2.6752 \cdot 10^8 sec^{-1} Tesla^{-1}. \tag{2}$$

The magnetic dipole $\vec{\mu}$ interacts with an external magnetic field $\vec{B_0}$, with the interaction energy ΔE defined by

$$\Delta E = -\vec{\mu} \cdot \vec{B_0}. \tag{3}$$

In a classical description, this interaction results in a parallel μ_+ or antiparallel μ_- orientation of the proton magnetic dipole in the external field $\vec{B_0}$.
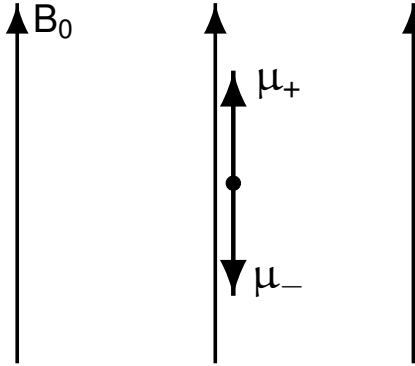
Abbildung 1: Proton magnetic dipole moment in external field $\vec{B_0}$.

A macroscopic sample containing N protons will populate the parallel and antiparallel state with occupation numbers N_+ and N_-, where $N = N_+ + N_-$. The occupation numbers N_+ and N_- follow Dirac statistics, but can here be approximated by a Boltzmann distribution,

$$N_\pm = N_0 e^{-\frac{E_0 \pm \Delta E}{kt}}. \tag{4}$$

Here, N_0 is a normalization factor. The parallel state is energetically favorable, hence $N_+ > N_-$. The surplus of protons in the parallel state leads to a macroscopic magnetization $\vec{M}$.

The magnetization can be calculated as the sum of magnetic dipole moments per unit volume,

$$\vec{M} = \frac{1}{V}\sum_i \vec{\mu_i} = \frac{1}{V}(N_+ - N_-)\,|\vec{\mu}|\,\vec{e_z}. \tag{5}$$

This sum can be evaluated and yields for the ground state magnetization $\vec{M}_0$

$$\vec{M}_0 = \frac{\mu N}{V} \, sinh(\mu B/kT) \, \vec{e_z}. \tag{6}$$

For weak fields (μB $<<$ kT), which is the case here, the sinh function (sinus hyperbolicus) can be expanded and the law of Curie follows:

$$\vec{M}_0 = \frac{N}{V} \frac{\hbar^2 \gamma^2 I(I+1)}{3kT} \vec{B}_0 \sim \vec{B}_0/T. \tag{7}$$

The macroscopic state characterized by a magnetization $\vec{M}_0$ parallel to the external magnetic field $\vec{B}_0$ as shown in Fig. 2 minimizes the energy.
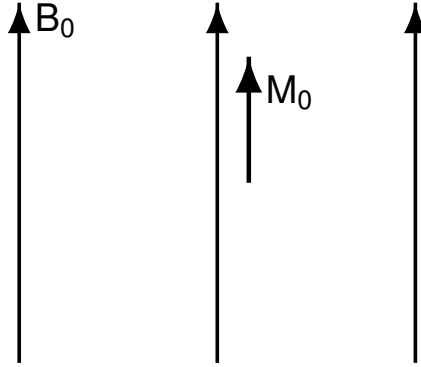
Abbildung 2: Ground state magnetization $\vec{M}_0$ along $\vec{B}_0$.

In general, the magnetization $\vec{M}$ can have an arbitrary direction relative to the external field.
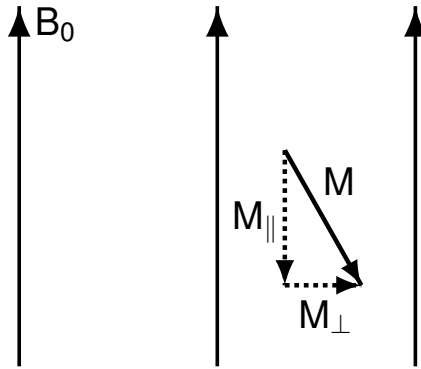
Abbildung 3: Parallel magnetization $\vec{M}_\parallel$ and transverse magnetization $\vec{M}_\perp$.

The magnetization $\vec{M}$ shown in Fig. 3 represents a macroscopic state different from the ground state. This state will therefore dissipate its excitation energy and reach the ground state

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asymptotically on a characteristic time scale. For further discussion, the magnetization $\vec{M}$ is decomposed into components $\vec{M}_{\parallel}$ parallel and $\vec{M}_{\perp}$ transverse to the external field. In particular, $\vec{M}_{\parallel}$ can be antiparallel to the external field $\vec{B_0}$.

The interaction between the external magnetic field $\vec{B_0}$ and the magnetization $\vec{M}$ as expressed by eq. 3 results in a torque $\vec{\tau}$ acting on the magnetization,

$$\vec{\tau} = \vec{M} \wedge \vec{B_0}. \tag{8}$$

This torque is zero if the magnetization and the magnetic field are parallel, as is the case for the ground state magnetization $\vec{M_0}$ in an external static field.

Inserting the components $\vec{M}_{\parallel}$ and $\vec{M}_{\perp}$ into eq. 8 shows that the torque is acting only on $\vec{M}_{\perp}$. Without relaxation processes, the rate of change of $\vec{M}_{\perp}$ is given by

$$\frac{d\vec{M}_{\perp}}{dt} = -\gamma \vec{M}_{\perp} \wedge \vec{B_0}. \tag{9}$$

The quantity $\frac{d\vec{M}_{\perp}}{dt}$ is perpendicular to $\vec{M}_{\perp}$ and $\vec{B_0}$, hence $\vec{M}_{\perp}$ precesses around $\vec{B_0}$. The angular frequency ω of this precession is called the Larmor frequency ω_L.
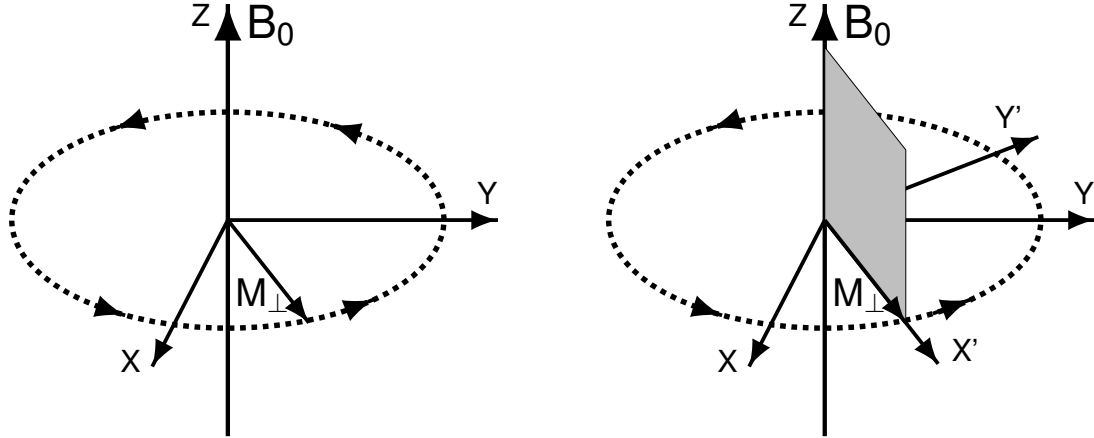
Abbildung 4: LEFT: Precession of $\vec{M}_{\perp}$ around $\vec{B_0}$.   RIGHT: Rotating reference system.

The precession of $\vec{M}_{\perp}$ in the (x,y)-plane is shown in Fig. 4 on the left. A rotating reference system with coordinates (x',y',z) is defined by the condition of the (x',y')-plane rotating in the (x,y)-plane, and by the requirement that $\vec{M}_{\perp}$ be pointing in x'-direction. In this rotating frame, the transverse magnetization $\vec{M}_{\perp}$ is constant in absence of relaxation processes, with (x',y')-components $\vec{M}_{\perp} = (M_{\perp},0)$. The total magnetization is defined by $\vec{M} = (M_{\perp},0,M_{\parallel})$.

A magnetization $\vec{M}_\perp$ transverse or $\vec{M}_\parallel$ antiparallel to $\vec{B}_0$ can be generated by applying a high frequency pulse to the ground state magnetization $\vec{M}_0$.
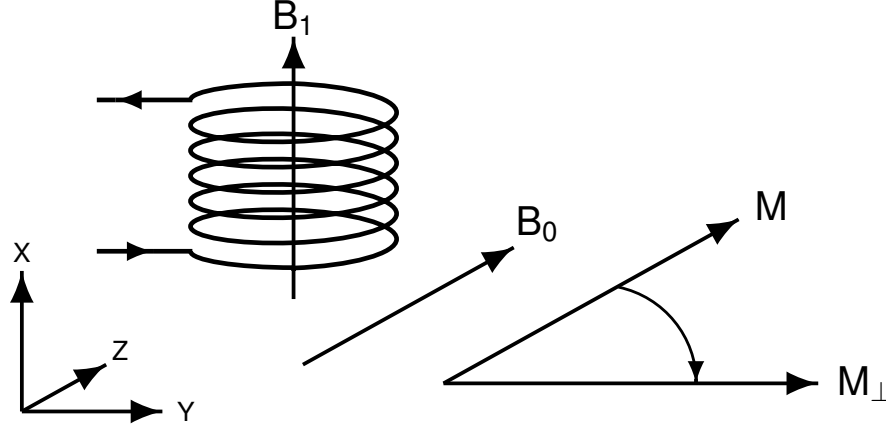
Abbildung 5: High frequency pulse along x-direction.

Consider the situation as shown in Fig. 5 above. The external static magnetic field $\vec{B}_0$ is pointing in z-direction. A coil is oriented along the x-direction. Applying a sinusoidal voltage of frequency ω_{HF} on the coil results in a solenoidal magnetic field $\vec{B}_1(t)$ which is longitudinally polarized along the x-direction. The external magnetic field is now the sum of the static field $\vec{B}_0$ plus the time dependent field $\vec{B}_1$. This external field is not parallel to the z-direction, and will therefore exert a torque on the ground state magnetization,

$$\vec{\tau} = \vec{M}_0 \wedge (\vec{B}_0 + \vec{B}_1(t)). \tag{10}$$

The time evolution of the magnetization now involves two precessions. The first precession around the z-axis is due to the static field $\vec{B}_0$, and defines the azimuthal angle of the magnetization. The high-frequency field $\vec{B}_1(t)$ induces a second precession around the x-axis. This precession defines the polar angle in the time evolution of the magnetization when applying the high-frequency pulse.

The time evolution of the magnetization due to the combined action of the static field $\vec{B}_0$ and the time dependent field $\vec{B}_1(t)$ is shown in Fig. 6. For pulse durations which are short as compared to the relaxation times, the magnitude of the magnetization is approximately constant, and the tip of the magnetization vector will move on a sphere with radius $|\vec{M}_0|$. The location on this sphere is defined by the azimuthal angle φ and the polar angle θ which arise from the two precessions explained above. In this spherical coordinate system, the magnetization $\vec{M}$ is expressed as $\vec{M} = (M \sin\theta \cos\varphi, M \sin\theta \sin\varphi, M \cos\theta)$. The angle φ is a function of time, $\varphi = \omega_L t$, with ω_L the Larmor frequency.

$$\omega_L = \gamma B_0, \tag{11}$$

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and with γ the gyromagnetic ratio defined in eq. 2. The angle θ is a function of time,

$$\theta = \gamma B_1 t. \tag{12}$$

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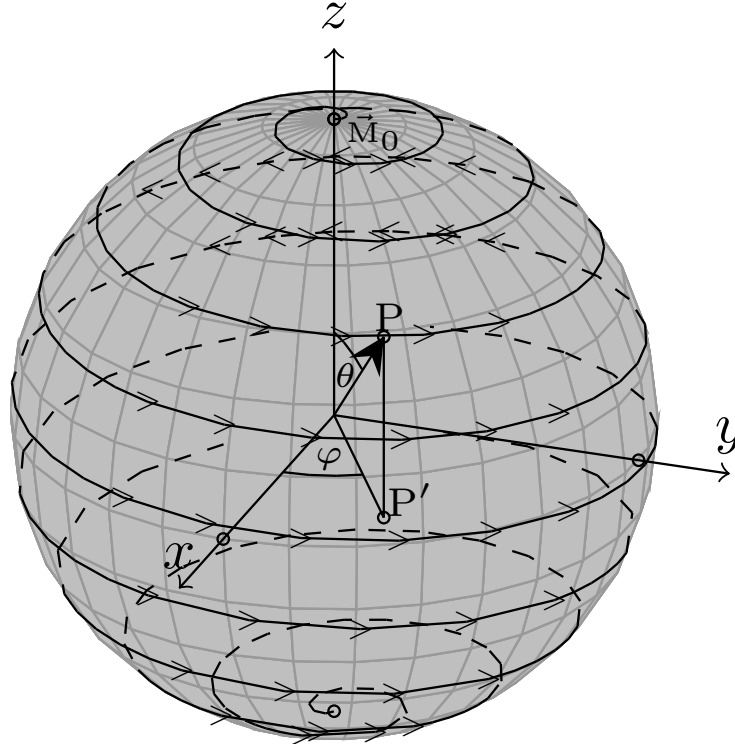
Abbildung 6: Time evolution of magnetization $\vec{M}$ during high-frequency pulse.

A pulse which generates a polar angle $\theta = 90^0$ is called a 90^0 pulse. Such a pulse transforms the ground state magnetization $\vec{M}_0$ into transverse magnetization $\vec{M}_\perp$, with $\vec{M}_\parallel = 0$. Similarly, a pulse resulting in a polar angle of $\theta = 180^0$ is called a 180^0 pulse. Such a pulse transforms the ground state magnetization $\vec{M}_0$ into an antiparallel magnetization $\vec{M}_\parallel$ = -$\vec{M}_0$, with $\vec{M}_\perp = 0$.

2 NMR Signal

2.1 Hardware

Make yourself familiar with the hardware by reading Appendix A and B. Remove the styrofoam shielding of the magnet and have a look inside.

2.2 Signal generation

The probes are located within the volume of the coil shown in Fig. 5 when the glass tubes are put into the magnet (see Fig. 16 of Appendix B). The high frequency pulses of frequency ω_{HF} are generated in the p20 electronic unit explained in Appendix A. These pulses act on the magnetization as illustrated in Fig. 6. After the pulse, the transverse magnetization $\vec{M}_\perp$ precesses around the z-axis. Due to this precessing magnetization, the magnetic flux through the coil is changing in time. The coil therefore generates an induction signal modulated by the Larmor frequency. This signal is fed back to the p20 electronic unit.
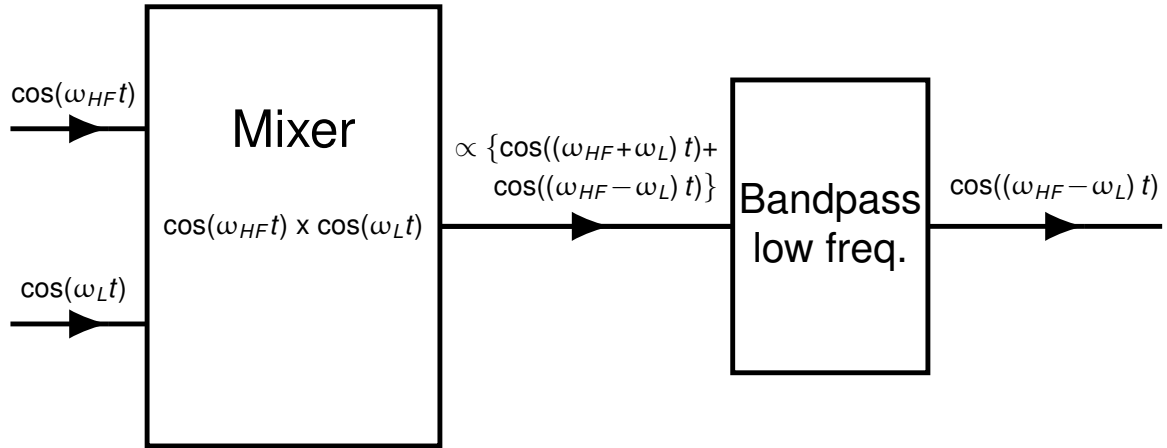
Abbildung 7: Creation of signal in p20 electronic unit.

The induction signal of the coil is mixed in the p20 electronic unit as illustrated in Fig. 7. This mixing involves a multiplication of the coil signal with the high-frequency signal ω_{HF}, which can, for example, be achieved by using an operational amplifier circuit. The output of the mixer can be calculated with the trigonometric formula for the product of two cosine terms. This product is the sum of two time dependent terms, one containing the difference, and the other the sum of the two input frequencies. Note that ω_{HF} is of fixed value $\omega_{HF} = 19.8$ MHz, whereas the Larmor frequency ω_L can be changed by turning the screw W1 of the magnet as explained in Appendix B. The difference between ω_{HF} and ω_L is on the order of a few hundred Hertz, and is called the working frequency. The frequencies of the two terms in the output of the mixer are therefore very different, one on the order of a few hundred Hertz, with the second frequency in the range of 40 MHz. A low frequency bandpass filter will transmit only the low frequency term. This signal of a few hundred Hertz is provided by the p20 electronic unit, and is available on the cable labeled **"Signal"**. Every time the p20 unit provides a signal on this cable, a standard trigger signal is provided on the cable labeled **"Trig"**. This trigger signal is of square form, with an amplitude of about 40 V, and duration ~ 4 μs. You can input this trigger signal on the second channel, or the external input, of the oscilloscope, and set the trigger parameters of the oscilloscope accordingly.

2.3   Calibration high frequency pulses

Before you can start with the measurements you need to define Puls I and Puls II as 90^0 and 180^0 pulse, respectively.

Find the box with the label **duplexer** which is sitting on the table above the electronics unit. This duplexer box has three connections:

- **Puls in**: This connector takes the high frequency pulse of the electronic unit.

- **Signal in/Puls out**: This cable connects the duplexer box with the connector C illustrated in the Appendix B of the magnet.

- **Signal out**: This cable transmits the induction signal of the coil back to the p20 unit.

Proceed in the following order to see the high frequency pulses on the oscilloscope:

- Make sure that the electronic unit does not produce any pulses. The OPERATE button of S1 has to be OUT and the S2 switch has to be in OFF mode (see Appendix A for meaning of S1 and S2).

- Find the attenuator box (cylindrical shape)with label **ATT U1** on the **Puls In** connector of the duplexer box. Unplug the cable which connects this attenuator box **ATT U1** with the p20 electronic unit where the cable carries the label **Duplexer Puls In**. Find the box (cylindrical shape) with label **ABSCHWAECHER 45,5 db**. Connect this box on the A side with the cable with label **Duplexer Puls In**. Take the cable on the B side of the 45,5 db attenuator and connect to the input of the oscilloscope.

- Generate pulses by pushing the OPERATE button into IN position and switch S2 into *"periodic"* mode. Select Puls I by pushing the Puls I button of the S1 switch. Generate 10 pulses per second by moving the S3 switch into the 100 ms position.

- Look at the high frequency pulse on the scope. Choose an appropriate time base and select the trigger mode by triggering on the input channel with positive slope and trigger threshold of about 2 V. What is the modulation frequency of this pulse? Change the switch S6 to minimum value. Convince yourself that the pulse duration is now minimum. Increase switch S6 slowly. Check on the scope that the pulse duration increases correspondingly.

- Repeat the same for Puls II. Select Puls II by pushing the Puls II button of the switch S1. Check the pulse duration by adjusting the S7 switch.

- Disable pulse generation by pushing the OPERATE button of S1 into OUT position and the S2 switch into OFF position.

- Reconnect the cables properly.

In order to define the 90^0 and 180^0 pulses proceed in the following order:

- Insert probe Gd600 into the magnet.

- Select Puls I on the S1 switch.

- Select one pulse every 3 seconds by an appropriate setting of the S3 switch.

- Generate pulses by pushing the OPERATE button of S1 into IN position and the S2 switch into *"periodic"* mode. Look at the signal on the scope. You expect a signal which is modulated by the working frequency ν_w. Choose a time base for a working frequency of $\nu_w = 1$ kHz. Connect the trigger cable **"Trig"** on the second channel of the oscilloscope (alternatively on the external trigger input), and select the trigger mode which is appropriate to how the trigger cable is connected. Trigger on positive edge with a threshold of about 2 V. Adjust the working frequency to 1 kHz by turning the screw W1 explained in Appendix B of the magnet.

- Increase the pulse duration of Puls I by increasing the value of switch S6. Watch the amplitude of the signal on the scope. When is Puls I a 90^0 pulse ?

- Repeat the same procedure for Puls II. Change the pulse length of Puls II by varying the switch S7. When is Puls II a 180^0 pulse?

3 Part I: Relaxation time

3.1 Bloch equations

In the rotating frame illustrated in Fig. 4, the transverse and longitudinal magnetization are constant if no relaxation processes take place. The relaxation processes result in a time dependence of the transverse and longitudinal magnetization. The time evolution in the rotating frame is decribed by the Bloch equations,

$$\frac{d\vec{M}_\perp^{rot}(t)}{dt} = -\frac{\vec{M}_\perp^{rot}(t)}{T_2}, \tag{13}$$

$$\frac{d\vec{M}_\parallel^{rot}(t)}{dt} = -\frac{\vec{M}_\parallel^{rot}(t) - \vec{M}_0^{rot}}{T_1}. \tag{14}$$

These equations assume that the time evolution is dominated by a restoring force which is linearly proportional to the deflection from equilibrium. The constant T_2 in eq. 13 is the spin-spin relaxation time whereas T_1 in eq. 14 is the spin-lattice relaxation time. The ground state magnetization is the same in the lab and in the rotating system, $\vec{M}_0 = \vec{M}_0^{rot}$.

The time evolution of the magnetization $\vec{M}$ in the laboratory system is related to the time evolution of magnetization $\vec{M}^{rot}$ in the rotating system by

$$\frac{d\vec{M}}{dt} = \frac{\partial \vec{M}^{rot}}{\partial t} + \vec{\omega} \wedge \vec{M}. \tag{15}$$

The Bloch equations in the laboratory system are hence written in the following way

$$\frac{d\vec{M}_\perp(t)}{dt} = \gamma(\vec{B} \wedge \vec{M})_\perp - \frac{\vec{M}_\perp(t)}{T_2}, \tag{16}$$

$$\frac{d\vec{M}_\parallel(t)}{dt} = \gamma(\vec{B} \wedge \vec{M})_\parallel - \frac{\vec{M}_\parallel(t) - \vec{M}_0}{T_1}. \tag{17}$$

3.2 Spin-spin relaxation T_2 by spin echo method

A transverse magnetization $\vec{M}_\perp$ represents a state which contains excitation energy. First, the interaction of the magnetic dipoles with the external magnetic field contributes according to eq. 3. This term is called the spin-lattice contribution. Second, the interaction energy of two magnetic dipoles depends on the orientation of the dipoles. The antiparallel orientation is energetically favorable. A transverse magnetization hence contains the corresponding interaction energy when many magnetic dipoles are oriented parallel to each other. This term is called the spin-spin contribution.

The time evolution of transverse magnetization is determined by the solution of eq. 16,

$$\vec{M}_\perp(t) = \vec{M}_\perp^0 e^{-\frac{t}{T_2}}. \tag{18}$$

After the 90^0 pulse the transverse magnetization will precess around the static field $\vec{B}_0$ with the Larmor frequency ω_L defined by eq. 11. Due to the inhomogeneity of the field, protons at different positions in the probe will precess with different Larmor frequencies. As a consequence, a phase difference between the protons will develop. This phase difference results in a dephasing of the transverse magnetization on a time scale much shorter than the relaxation time T_2. A 180^0 pulse reverts the phases, and can be used for correction.
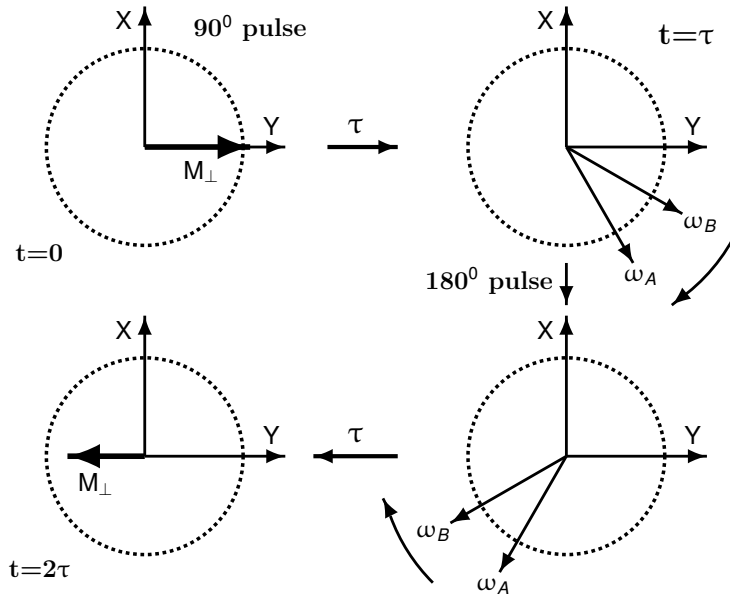

Abbildung 8: Dephasing of transverse magnetization $M_\perp$.

Consider the pulse sequence 90^0-180^0 as illustrated in Fig. 8. A 90^0 pulse at time t=0 generates a transverse magnetization $\vec{M}_\perp$ along the y-axis. Protons at different locations of the magnetic field will have slightly different Larmor frequencies due to the inhomogeneity of the field. Assume that the magnetic field is larger at location A than location B, hence $\omega_A > \omega_B$. Protons at location A precess with frequency ω_A, whereas protons at location B precess with frequency ω_B in clockwise fashion. At time t=τ, the protons at locations A and B have acquired a phase difference. The protons at location A are ahead in phase compared to the protons at location B as illustrated in the upper right corner of Fig. 8. A 180^0 pulse is applied at time t=τ. This pulse rotates the magnetic dipoles by 180^0 around the x-axis. After this 180^0 pulse, the dipole orientation of the protons at locations A and B is reversed. The protons at location B are now ahead of the protons at location A as shown in the lower right corner. The time duration of the 180^0 pulse is short as compared to the time τ, and can therefore be neglected. The protons continue to precess clockwise after the 180^0 pulse. After another time interval τ, the protons at A and B are in phase again as illustrated in the lower left corner. All the magnetic dipoles in phase build up the magnetization $\vec{M}_\perp$ at time t=2τ.

Select a pulse sequence I-II on pushbutton S1 and τ=10 ms on switch S4 and a repetition rate of 1/3 Hz on S3. Insert probe Gd600 into the magnet and activate the pulse sequence. Watch the signal on the scope.
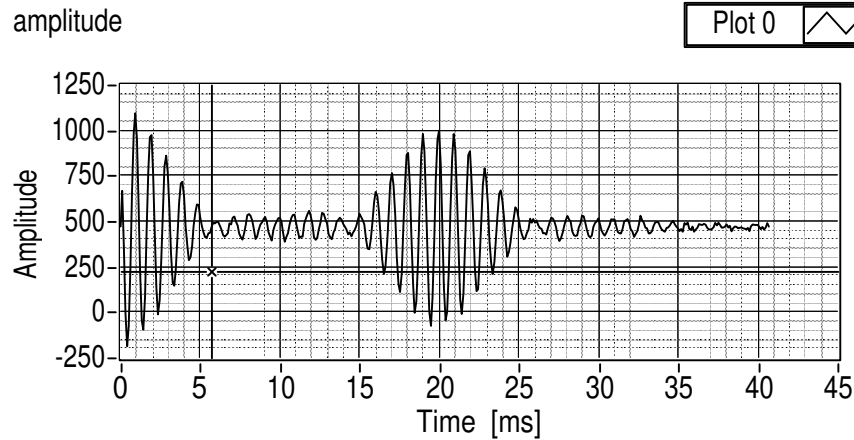
Abbildung 9: Pulse sequence 90^0-180^0 with τ=10 ms.

Fig. 9 displays the NMR signal of pulse sequence I-II with τ=10 ms. The decay of the transverse magnetization due to loss of coherence (dephasing) as explained above is visible at times t < 5 ms. At later times, the spin echo is visible in the time range 15 ms < t < 25 ms. This spin echo is modulated by the working frequency as illustrated in Fig. 7. The strength of the spin echo is represented by the area enclosed by the signal. The evaluation of this signal strength in the time domain would necessitate the determination of its envelope. Alternatively, due to Parseval's theorem, the signal strength can be evaluated in the time conjugate variable, the frequency. In the frequency domain, the spin echo is represented by an approximate Gaussian profile, which can be integrated numerically. The decay curve of eq. 18 can be measured at different times by varying the parameter τ in the pulse sequence I-II.

The spin echo method described above has limitations when measuring the decay curve at large times. For such measurements, 2τ is large hence also τ is large. Due to molecular diffu-

sion, the protons can move to different locations before the 180^0 pulse is applied. The average Larmor frequencies in the time intervals $0 < t < \tau$ and $\tau < t < 2\tau$ can hence be different due to field inhomogeneities. The magnetic dipoles are in such case only approximately aligned along the negative y-axis at time t=2τ as shown in Fig. 8, and only partial coherence is achieved. This limitation leads to reduced signals with a correspondingly reduced value for the relaxation time T_2.

3.3 Spin-spin relaxation T_2 by Carr-Purcell sequence

The Carr-Purcell sequence minimizes the effects of molecular diffusion and field inhomogeneities, and hence improves the limitation of the spin echo method described above. The Carr-Purcell sequence starts with a 90^0 pulse to generate a transverse magnetization. A 180^0 pulse is applied after a small time interval τ, which leads to phase coherence of the system at time t=2τ as illustrated in Fig. 8. The system then starts to loose the coherence again due to field inhomogeneities. At time t=3τ another 180^0 pulse is applied hence the system is phase coherent at time t=4τ. This pattern of phase coherence at even multiples of τ, and generation of 180^0 pulses at odd multiples, repeats to large times as shown in Fig. 10. A measurement of the spin-spin relaxation time by the Carr-Purcell method hence yields a value which is closer to the true value of the system as compared to the measurement with the spin echo method.
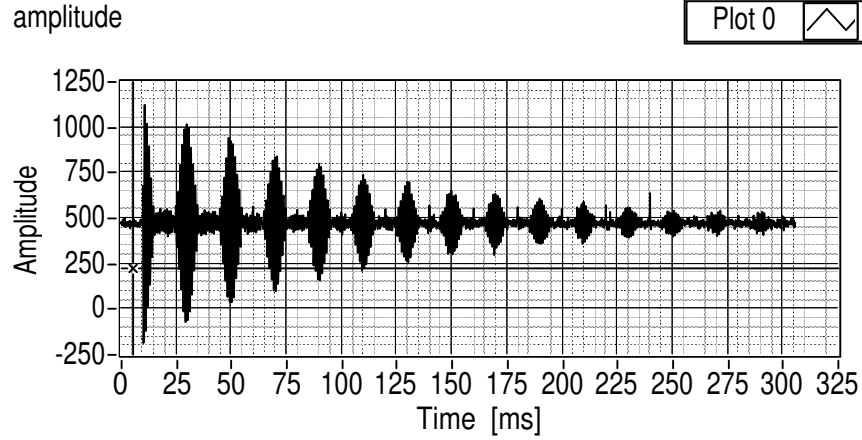
Abbildung 10: Carr-Purcell sequence with τ=10 ms.

3.4 Spin-lattice relaxation T_1

The spin lattice measurement starts with the generation of a 180^0 pulse. Such a pulse produces a magnetization antiparallel to the external $\vec{B}_0$ field. This magnetization will undergo a time evolution as described by the solution of eq. 17,

$$\vec{M}_\parallel(t) = \vec{M}_0(1 - 2\,e^{-t/T_1}).\tag{19}$$

The longitudinal magnetization $\vec{M}_\parallel$(t) does not produce a signal. A 90^0 pulse at time t will, however, transform $\vec{M}_\parallel$(t) into a transverse magnetization which induces a signal in the coil.

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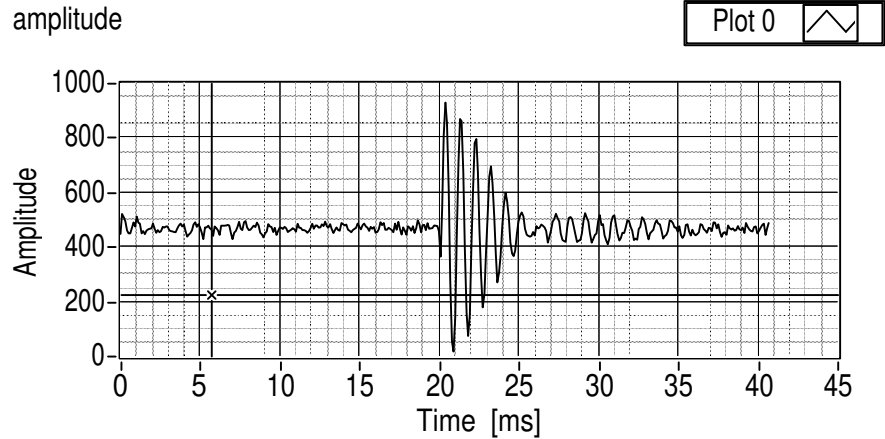
Abbildung 11: Pulse sequence 180^0-90^0 with τ=20 ms.

The signal from a pulse sequence 180^0-90^0 with a value τ=20 ms is shown in Fig. 11. The signal at time t=τ is proportional to the longitudinal magnetization $\vec{M}_\parallel$ at time t=τ. The decay curve of the longitudinal magnetization $\vec{M}_\parallel$(t) can be measured at different times by varying the value of τ in the pulse sequence 180^0-90^0.

3.5   Measurements of relaxation times

3.5.1   Measurement T_2 by spin echo method

Measure about 8-10 points of the decay curve given by eq. 18 by using the pulse sequence I-II and by choosing appropriate τ values. Use the LabVIEW application *"T2_meas_freq.vi"* for these measurements. You can find this program in the folder *"F61/sw"* which you can select by following the link *"sw-Verknüpfung"* on the desktop of the PC. You can initialize this LabVIEW program by double left click on its icon in the folder *"F61/sw"*. The front panel of *"T2_meas_freq.vi"* will open, displaying the different elements of the program with a black grid on grey background. The boxes shown in white color are input fields where you need to fill in information which is needed to do the measurement. The boxes in light grey color are output fields displaying the numerical value of parameters which have been calculated by the program.

The information of the measurements is stored in a file. Each F61 group gets a folder for storing these files. Find the link to the folder *"ss20"*/*"ws20"* on the PC desktop. Here, *"ss20"*/*"ws20"* denotes summer semester 2020, or winter semester 2020/2021, respectively, with a corresponding labeling for the following years. In this folder *"ss20"*/*"ws20"*, create a new folder and rename this folder by your starting day of the experiment, in accordance with other already existing folders. Enter the name of your folder in the *"folder"* input field at the top of the LabVIEW program, and specify a name for the data file of the measurement. The input field *"scan freq"* specifies the frequency with which the signal is scanned on the data acquisition card in the PC. By default, the scanning frequency is set to 10 kHz which results in 10 data points per oscillation period of the signal.

The LabVIEW program consists of a main program, and several subprograms. You can start the main program by left click on the right arrow which is located on the left in the top icon list of the front panel. When starting the main program, all the input fields of the front panel are read, and the corresponding variables are initialized. The background of the front panel is changing from black grid on grey to uniform grey. The main program can be stopped by left click on the button **"STOP"** (in red) in the top left of the front panel.

The main program contains the following subprograms:

1. **Single measurement**:

   Enter the time period for measuring the signal in the field *"meas time"* (units of ms). Start this subprogram by clicking on *"GO"*. The data points are displayed on the leftmost of the three graphic panels labeled *"amplitude"*. Convince yourself that your measurement is not in conflict with what you expect from your chosen pulse parameter settings of the p20 electronic unit. You can zoom into the region of the spin echo signal by entering values in the field *"spin echo time"* and *"ΔT (+-)"* (units of ms). Choosing "spin echo time" = 400 ms, and "ΔT(+-)" = 10 ms will, for example, define a zoom range from 390 ms to 410 ms. Run the subprogram again. The chosen zoom range is now displayed in the middle display labeled *"amplitude window"*.

   CAUTION: The input fields are managed by the main program. When you change the value of any of these input fields, a sign $\sqrt{}$ appears on the very left in the top icon list. This sign is a notification that you need to tell LabVIEW to update the input parameters. You can do so by left click anywhere on the background of the front panel. The sign $\sqrt{}$ will disappear.

   As explained above, the strength of the spin echo signal can be evaluated in the time domain, or in the frequency domain. The rightmost of the three panels of this subprogram displays the Fourier transformed signal of the zoom range shown in the middle panel. In the frequency domain, the signal has an approximate Gaussian profile which should be centered close to the value of the working frequency, $\nu_w = 1$ kHz. If needed, readjust the working frequency such that this Gausssian profile is centered at $\nu_w = (1000 \pm 50)$ Hz. The signal strength is determined by summing up the bin contents over the range of this Gaussian profile. Use the two cursors in this panel to define this range. Move the left cursor (orange color) to the left, and the right cursor (green color) to the right of the signal range. Don't put the cursor very tight at the edges of the Gaussian profile, leave about 50 Hz on either side. Proceed with the *"many measurements"* when you are convinced that all parameters for this measurement are set properly.

2. **Many measurements**:

   The signal to noise ratio can be improved by averaging over many measurements. For averaging over ten measurement, enter the value "10" in the field *" number meas"*, then click *"GO"*. The program displays the average and an associated error in the output fields *"avg peak"* and *"error avg peak"*, respectively, when the ten measurements are done.

3. **Write data to file, update plot**:

   Write the measured data point to the file by clicking *"GO"*. The program shows the updated contents of the file and the updated plot. The ranges of the X and Y-axis can

be defined in the input fields *"X-range"* and *"Y-range"*, respectively. If you have chosen new values for either one of these ranges, proceed with the next subprogram to display the data within the new range.

4. **Update plot, no fit**:

   This subprogram reads the information from the data file, and updates the plot of the measured data points within the X and Y-range as defined in the corresponding input fields. If a data point has been entered erroneously in the data file, then the information of this data point can be erased by removing the corresponding line in the data file. Click *"GO"* for updating the plot and the display of the file content.

5. **Fit**:

   This subprogam fits your measured data points with a function defined by eq. 18. Click *"GO"* for executing the fit. The fit value of T_2 and an associated error are shown.

The information of this relaxation time measurement is displayed on the front panel. You can print the front panel on the F61 printer, and add this printout to your notes in your lab book.

3.5.2 Measurement T_2 by Carr-Purcell sequence

The measurement of T_2 by the Carrr Purcell sequence is done with *"CP_meas_freq.vi"*. This program consists of a main program and several subprograms, similarly as for the T_2 measurement by the spin-echo method. The start and stop of the main program, as well as the input fields of the main program, are identical to the measurement by the spin-echo method.

The main program has three subprograms:

1. **Single measurement:** Enter the time during which you want to measure the Carr-Purcell sequence in the input field *"meas. time"* (units of ms). A measuring time of 600 ms will give you a first impression of such a Carr-Purcell sequence. Define the parameter τ for the Carr-Purcell sequence with the S4 switch of the P20 unit such that about 6-8 spin echos are visible. In the Carr-Purcell sequence, the measured spin echos are equidistant in time. At early times, the spin echos are clearly visible, while at later times the spin echos decrease according to eq. 18. Similarly as for T_2 in the spin echo measurement, a zoom range be defined by values in the input fields *"spin echo time"* and *"$\Delta T(+-)$"* (units of ms). Use the zoom option to find the latest (and weakest) spin echo visible in this Carr-Purcell sequence. Enter the number of spin echos you want to measure in the input field *"nr of SE"*, and the times at which the spin echos are visible in the input vector field labeled *"SE time"*. Adjust the 600 ms measuring time if necessary. Proceed with the next subprogram when all the parameters are set properly.

2. **Many measurements:** This subprogram evaluates the spin echos within the time intervals defined by the input vector field *"SE time"* and *"del T(+-)"*. Enter a value of "10" in the input field *"number meas"* for averaging over ten measurements. The averages over the ten measurements are displayed together with the associated error. These data points are plotted in the panel XY graph. The range over which the panel is displayed can be defined in the input fields "X-range" and "Y-range". Run the subprogram "update plot" for displaying the panel within a modified range.

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3. **Update plot:** This subprogram updates the graphics panel of the measured data points within the ranges as defined in the input fields "X-range" and "Y-range".

4. **Fit:** This subprogam fits your measured data points with a function defined by eq. 18. The fit value of T_2 and an associated error are shown.

3.5.3   Measurement T_1

The measurement of the T_1 relaxation time is done by *"T1_meas_freq.vi"*. This LabVIEW application follows the same structure as the one for the T_2 measurement by the spin echo method (*"T2_meas_freq.vi"*), except that the fitting routine is now defined by eq. 19.

3.6   Systematics of relaxation times

Proceed with the measurements of the relaxation time T_2 by spin echo and Carr-Purcell sequence and relaxation time T_1 for both probes Gd500 and Gd600. Write your measurements with associated errors in a table and discuss the systematics of your results.

4 Part II: Chemical shift

The Larmor frequency ω_L is given by eq. 11. If protons are bound in a molecule then the total magnetic field $\vec{B}_{tot}$ determines the Larmor frequency. This total field consists of the external field $\vec{B}_0$ and a contribution $\delta\vec{B}$ due to the electron orbitals,

$$\delta\vec{B} = -\sigma\vec{B}_0. \tag{20}$$

The contribution $\delta\vec{B}$ is proportional to the external field $\vec{B}_0$ and, according to Lenz's rule, opposite in sign. The proportionality factor σ represents the magnetic shielding of the external field $\vec{B}_0$. This shielding factor characterizes the molecule and each nucleus within the molecule. If the modified Larmor frequency is measured then this shielding factor σ can be determined,

$$\omega_i = \omega_L(1 - \sigma_i). \tag{21}$$

Here, ω_L denotes the free Larmor frequency and ω_i the frequency modified by the chemical shift. For identifying substances by the chemical shift, a reference substance is added.

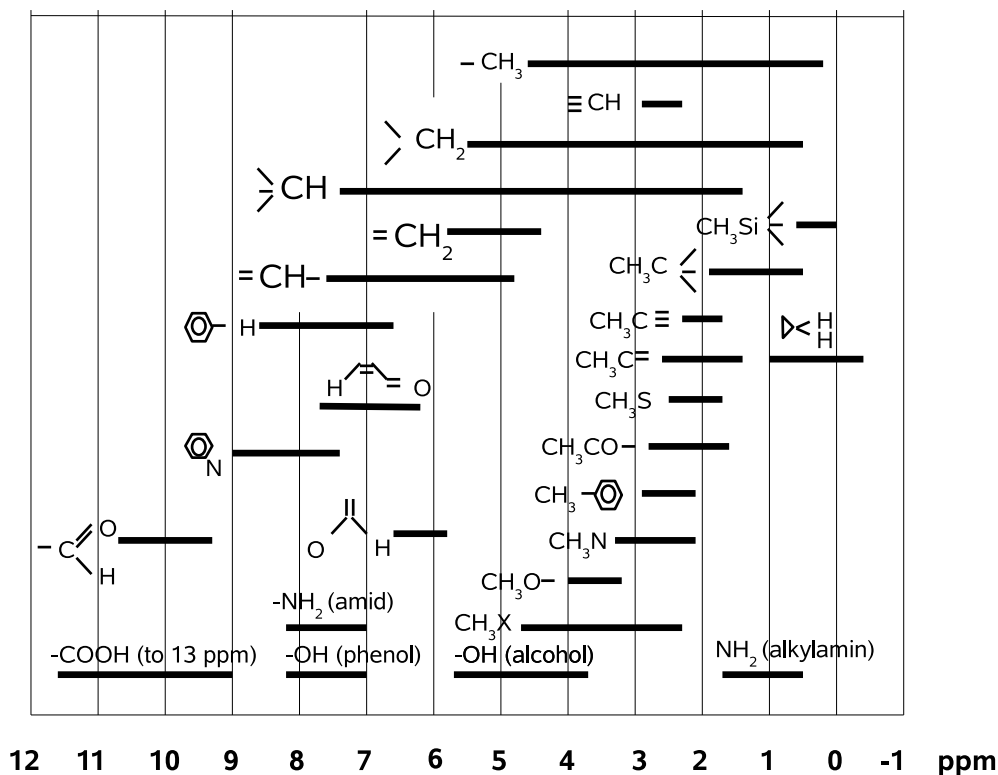Abbildung 12: Chemical shifts δ_i of compounds relative to TMS.

In Fig. 12, the proton chemical shift δ in organic compounds relative to the reference substance Tetra-Methyl-Silan (TMS) is shown in units ppm (part per million),

$$\delta_i = \sigma_i - \sigma_{TMS} = \frac{\omega_L - \omega_i}{\omega_L} - \frac{\omega_L - \omega_{TMS}}{\omega_L} = \frac{\omega_{TMS} - \omega_i}{\omega_L}. \tag{22}$$

4.1 Measurement chemical shift

Measure the chemical shift in the five probes A,B,C,D and E. Associate each probe with one of the substances listed in Fig. 13.
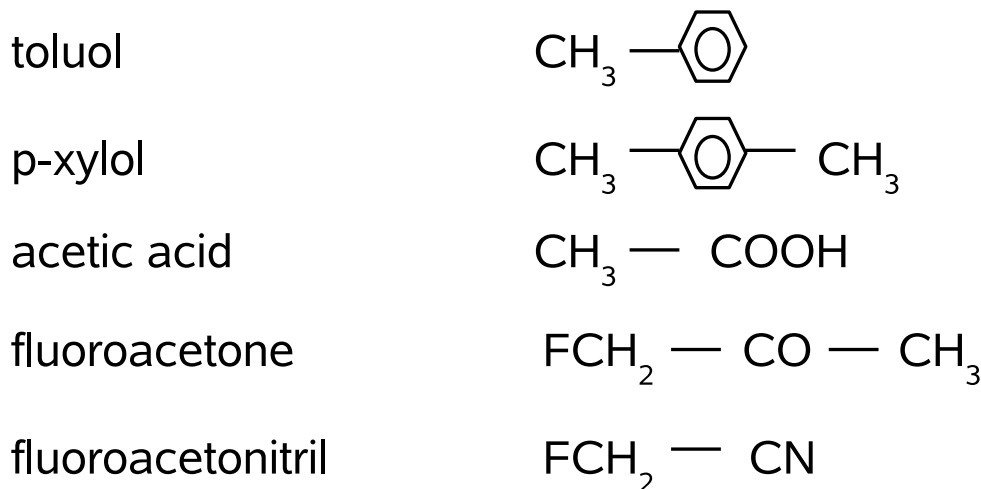
toluol CH_3 —⬡

p-xylol CH_3 —⬡— CH_3

acetic acid CH_3 — COOH

fluoroacetone FCH_2 — CO — CH_3

fluoroacetonitril FCH_2 — CN

Abbildung 13: Five substances for identification.

Each probe exists with a label "+", for example there is a probe D and a probe D+. The label "+" signifies that the reference substance TMS is contained in the probe. The Larmor frequency of the reference substance TMS can be identified by comparing the measurement of the probe with the measurement of the probe plus reference. The evaluation of the Larmor frequency ω_i relative to the reference gives the chemical shift δ_i expressed in eq. 22.

Use the measured chemical shifts δ_i to identify the five substances of Fig. 13 based on the information listed in Fig. 12. Toluol and p-xylol have the same chemical shifts. Use the intensity of the measured frequency response to separate these two substances.

Use the LabVIEW application *"chem_shift.vi"* to measure the chemical shifts. This application consists of a main program and two subprograms. The start and stop of the main program, as well as the definition of the input fields of the main program, are identical to the T_1 and T_2 measurements.

- **Meas**: This subprogram measures the NMR signal of the probe, and displays the data points in the left panel labeled *"Amplitude"*. The Fourier transform of the time signal is calculated in steps of 2 Hz and displayed in the right panel labeled *"Fourier transform"*. The information of the Fourier transform is saved in the data file which is specified in the input field *"data file"*. In general, it is good practice to choose a file name which reflects the name of the measured probe. Run this subprogram by clicking on *"GO"*. You can check the information of the data file by opening it with a text editor. The file contains two columns. The first column represents the frequency values in steps of 2 Hz, and the second column the corresponding intensity in arbitrary units.

- **Fit**: This subprogram reads the information in the data file, and displays the data in the panel labeled *"Frequency spectrum"*. The value of the measured Larmor frequencies can be determined much more accurately than the discrete Fourier step of 2 Hz by fitting the profile of the frequencies with a Gaussian. You need to define the range for these fits. Move the cursor (red color) of the panel to the maximum of the signal intensity, then read off the X-position of the cursor from the cursor window located above the graphics panel. Translate this cursor position into the closest multiple of 2 Hz. Specify the low edge of the window by subtracting 6 Hz from this center value, and the high edge by adding 6 Hz. With this procedure, the Gaussian fit will take into account a total of seven measured data points. Enter the low edge value in the field *"W1-low"*, and the high edge value in the field *"W1-high"*. Run the subprogram. The location of the fitted maximum is displayed in the output field *"peak1 [Hz]"* (units of Hertz). The field *"ppm1"* displays the same information but in units of ppm.

  A maximum of four peaks can be fitted simultaneously.

Use the 90^0 pulse for this measurement, and adjust the working frequency to $\nu_w = (500 \pm 50)$ Hz. Select the 90^0 pulse with a repetition rate of $1/3$ Hz to generate the response of the probe. To get familiar with this measurement, insert the probe Gd600 into the magnet. Take a measurement. You should see intensity in the Fourier transform at around 500 Hz.

- Over what interval is this intensity distributed?

- What determines this width?

- Use the pressure air as explained in Appendix B to put probe Gd600 into rotation. Repeat the measurement. Has the width of the frequency response changed?

Proceed with the measurements by putting the probes A-E into the magnet. Use the pressure air for accurate measurements.

- Identify the substances.

- Do the peaks you measure correspond to what you expect?

5 Part III: Imaging with NMR

The imaging measurements are made with the new Bruker NMR analyzer mq7.5. In order to carry out measurements which contain information on the position of the produced NMR signal, a magnetic field is necessary which has a position dependence. In practice, gradient fields are used for one, two and three dimensional imaging measurements. The gradient fields are superimposed to the static field $\vec{B_0}$ which defines the z-direction.

The gradient fields $\vec{B^x}, \vec{B^y}, \vec{B^z}$ are defined such that the field vector points in z-direction, and the strength of the field is linearly increasing as function of the corresponding coordinate.

$$\vec{B_0} = (0, 0, B_0)$$

$$\vec{B^x} = (0, 0, G^x \cdot x)$$
$$\vec{B^y} = (0, 0, G^y \cdot y)$$
$$\vec{B^z} = (0, 0, G^z \cdot z)$$

A gradient field can be produced by an arrangement of coils. For three dimensional imaging, three coil systems are needed which can switch the gradient fields $\vec{B^x}, \vec{B^y}, \vec{B^z}$ independently. In the Bruker NMR analyzer mq7.5, the three coil systems are mounted on an insert which is fixed by two screws in between the two pole pieces which define the static field $\vec{B_0}$.

Open the cover of the magnet unit and have a look inside. You will see the tip of one of the coil systems. On the desktop of the PC, you find a link "Bruker_pict". In the corresponding folder you find some pictures of the coil insert which carries the three coil systems.

5.1 One dimensional imaging

In one dimensional imaging, the position dependence of the NMR signal is generated by applying a gradient field which has a dependence in the corresponding direction, and the Larmor frequency hence becomes position dependent. In the following, we discuss one dimensional imaging along the z-direction.

5.1.1 Frequency coding

In one dimensional imaging along the z-direction, a gradient field $\vec{B^z}$ is superimposed to the static field $\vec{B_0}$. The Larmor frequency hence becomes z-dependent

$$\omega_L(z) = \gamma(B_0 + G^z \cdot z) = \omega_L^0 + \omega_z \tag{23}$$

For further discussion, we consider the rotating frame introduced in Fig. 4. In this frame, $\vec{M}_\perp$ is given by eq. 17 and denoted $\vec{M}_\perp^{rot}$. The transverse magnetization at a given z-position precesses with a Larmor frequency defined by eq. 10 and can thus be written as

$$M_\perp(z, t) = M_\perp^{rot}(z, t)\, e^{i\gamma(B_0 + G^z z)t} \tag{24}$$

The produced NMR signal is defined by

$$S(t) \propto \int_V M_\perp(z,t)\, e^{-i\omega_{HF}t} dV = \int_V M_\perp^{rot}(z,t)\, e^{i(\omega_L^0 + \omega_z - \omega_{HF})t} dV$$

$$= e^{i\Omega t} \int_z \left[\int_x \int_y M_\perp^{rot}(z,t) dx dy \right] e^{i\omega_z t} dz \qquad (25)$$

If the signal acquisition time T is much smaller than the relaxation time T_2, then the transverse magnetization $M_\perp^{rot}(z,t)$ is constant during readout and can be set as $M_\perp^{rot}(z)$. The measured NMR signal $S(t)$ is therefore, apart from the phase factor $e^{i\Omega t}$, the one dimensional Fourier transform of the transverse magnetization $M_\perp^{rot}(z)$. The quantity of interest, the magnetization $M_\perp^{rot}(z)$, can therefore be deduced by a one dimensional Fourier transformation of the measured NMR signal $S(t)$.

In practice, the NMR signal $S(t)$ is sampled at times $t_n = n\Delta t$ and hence yields a set of N data points

$$S_1 = S(\Delta t), \quad S_2 = S(2\Delta t,), \dots, \quad S_N = S(N\Delta t) \qquad (26)$$

A discrete Fourier transformation of the N data points S_N will result in N data points M_N defined by

$$M_1 = M_\perp(\Delta z), \quad M_2 = M_\perp(2\Delta z), \dots, \quad M_N = M_\perp(N\Delta z) \qquad (27)$$

with Δz defined by

$$\Delta z = \frac{Z}{N} = \frac{2\pi}{\gamma G^z N \Delta t} \qquad (28)$$

Here, Z denotes the full range of the position measurement.

5.1.2 Phase coding

In the frequency coding approach described above, the NMR signal is measured as a function of time. During the readout time, the Larmor frequency at a given position z is determimed by the applied gradient field, and the transverse magnetization precesses due to the gradient field by an amount

$$\Delta\phi(z) = \phi(z) - \phi(z=0) = (\gamma G^z z)t = \omega_z t \qquad (29)$$

During the readout the position information is contained in the phase angle as described by eq. 28. The phase angle can, however, also be varied by applying a gradient field which is of

constant duration but whose strength is increased in steps of ΔG^z. This equivalent approach is called phase coding.

Phase coding is achieved by applying a gradient field $B^z = G^z z$ during a time interval T_{Ph} before readout of the NMR signal. The phase acquired at position z during this time interval T_{Ph} is given by

$$\varphi(z) = (\gamma G^z T_{Ph})z = k_z z \tag{30}$$

The parameter $k_z = \gamma G^z T_{Ph}$ is the position frequency. After the phase coding gradient is switched off, all components of the transverse magnetization precess with the original Larmor frequency $\omega_L^0 = \gamma B_0$ but with a different phase angle which depends on the z-position. In phase coding, the different components all contribute to the NMR signal with the same frequencey but with different phases. The NMR signal is now defined by

$$S(k_x, t_0) \propto \int_V M_\perp(z, t_0)\, e^{-i\omega_{HF}t_0} dV = e^{i\Omega t_0} \int_z \left[\int_x \int_y M_\perp^{rot}(z, t_0) dx dy \right] e^{ik_z z} dz \tag{31}$$

The measurement of the phase coded NMR signal consists in making N measurements with different position frequencies $k_n = n\Delta k$ ($1 \leq n \leq N$). As expressed in eq. 30, the phase coded NMR signal only needs to be measured at time t_0. After the measurements, a set of N data points exists

$$S_1 = S(\Delta k, t_0), \;\; S_2 = S(2\Delta k, t_0), ..., \;\; S_N = S(N\Delta k, t_0) \tag{32}$$

As in frequency coding, the magnetization $M_\perp^{rot}(z)$ is deduced by a one dimensional discrete Fourier transformation of the measured data points S_N.

The two methods decribed above, frequency coding and phase coding, are mathematically equivalent. They differ, however, in the time required for the data acquisition. In frequency coding, the data points $S_n = S(t_n)$ as expressed in eq. 25 can be recorded in one sequence. In phase coding, N sequences are necessary to record the data points S_N as expressed in eq. 31.

5.1.3   One dimensional imaging measurements

The Bruker minispec mq7.5 is fully computer controlled by a graphical user interface. Your tutor will show you how to start the interface. The available application programs are listed in the top right corner of the interface in the folder *"minispec Applications"*. Double click on the application *"profile"* for a one dimensional imaging measurement. A graphics panel *"profile"* will open which contains the display of the measurement.

To start the measurement, left click on the blue icon *"Measure"* (bottom left corner). A menue *"Application Configuration Table"* will open. In this menue, the gradient directions are displayed on the left whereas the profile parameters are shown on the right. Choose the Y-gradient for a measurement in vertical direction. The pulse parameters contain default

values which in general don't need to be modified. Click on the *"OK"* button in bottom left of the panel after you marked the box *"Y-gradient"*. The *"profile"* application is programmed such that a measurement is taken every ten seconds. This measurement is made when the timer displayed in the lower left corner has reached zero. Click *"STOP"* for stopping the measurement. The data points of every measurement are stored in a data file. The file name contains a label which denotes the number of the measurement. These files *"testProfilxx.txt"* (xx = 1,2,3,..) are written into the folder *"C:/minispec/imagingdata"*. You can find this folder by clicking on the link *"imagingdata"* on the desktop.

You have to save the data files of the measurements which you want to display. Click on the link on the desktop *"ss20"*. Here, *"ss20"* denotes the summer semester 2020. For later semesters, a corresponding link will exist. In that folder, create your own folder and rename this folder identical to your data folder of the relaxation time measurements. Copy the files you want to display to your own folder, and rename the files such that you recognize the measurement by the file name.

5.1.4   One dimensional data display

A LabVIEW application *"many_profiles.vi"* is available for reading back data files for display. You can find this LabVIEW application by clicking on the link *"day3"* on the desktop. With the application *"many_profiles.vi"*, you can superimpose many measurements by reading back the corresponding data files from your folder. In general, the file names contain a common prename, a label denoting the number of the measurement, and a common postname. Enter the corresponding information in the front panel of *"many_profiles.vi"*. The different file numbers are entered in the input vector field *"file nr"*. The strings *"common prename"*,*"file nr"* and *"common postname"* are concatenated for defining the full name of the file which is read. Enter the number of files which should be read in the input field *"XXX"*. You can read back and display only one file by leaving the input field *"file nr"* empty, such that the strings *"common prename"* and *"common postname"* concatenate to the full file name.

5.1.5   One dimensional measurements

Make the following one dimensional measurements in vertical direction::

- Take the glass tube which is filled with about 15 mm of oil. What signal do you expect? The ring on the glass tube should be positioned such that the oil is centered around the zero position in vertical direction. If necessary, adjust the position by turning the ring with respect to the glass tube, and moving it into the correct position.

- Take the glass tube which is filled with about 50 mm of oil. In this measurement, you can see the effects of the nonlinearity of the gradient field. From this measurement, estimate in which vertical range the probe has to be located for minimizing the effect of nonlinearity of the gradient field.

- Take the glass tube which contains the teflon structure immersed in oil. What signal do you expect? (Teflon material does not produce a NMR signal)

- Take an empty glass tube, fill it with about 15 mm of sand, and add approximately 4 mm of oil on top. Put the glass tube into the magnet, and measure until you cannot see any changes from one measurement to the next. Superimpose some of the measurements in the LabVIEW display in order to illustrate the time development of the system. Can this process of oil mixing with sand be understood as a diffusion process?

  Consult Appendix C for some basic information on diffusion processes.

5.2 Two dimensional imaging

Two dimensional imaging measurements can be made by a two dimensional Fourier method. In this approach, a slice is first selected by an appropriate combination of gradient field and high frequency pulse. Within the slice, two dimensional position information is derived by a combination of frequency and phase coding.

5.2.1 Slice selection

A slice in z-direction is defined by the property that the z-coordinate of all the points within the slice satisfy $z_1 \leq z \leq z_2$. If a gradient field B^z is switched on, then every z-position is characterized by a Larmor frequency as defined by eq. 22. The positions z_1 and z_2 are characterized by frequencies ω_1 and ω_2, respectively. If the high frequency pulse $F(\omega)$ contains only frequencies ω such that $\omega_1 \leq \omega \leq \omega_2$, then the slice $z_1 \leq z \leq z_2$ will be selectively excited. Such a pulse $F(\omega)$ corresponds to a sinc pulse in the time domain

$$f(t) \propto \frac{sin(at)}{t} \tag{33}$$

After the sinc pulse of duration t_p, the slice $z_1 \leq z \leq z_2$ contains excitation energy. The Larmor frequency is different for subslices at different z-positions when the slice selection gradient is switched on. The different subslices are therefore out of phase after the high frequency pulse. This dephasing can be compensated by switching on the slice selection gradient with reversed polarity for a time interval $t_p/2$ after the high frequency pulse. This additional gradient is called the slice refocussing gradient.

5.2.2 Two dimensional Fourier method

Within the selected slice, the two dimensional position information can be derived by a combination of phase coding in x-direction and frequency coding in y-direction. The imaging sequence is repeated N times for different values of the phase coding gradient $G_n^x = n\Delta G^x$ $(1 \leq n \leq N)$. In each sequence, the NMR signal is read out at times t_m with the readout gradient G^y switched on. For each combination (k_n, t_m) of the parameters $k_n = n\gamma\Delta G^x T_{Ph}$ and $t_m = m\Delta t$ a data point $S(k_n, t_m)$ exists. From this matrix of $N \times M$ data points, the two dimensional matrix of the image can be derived by a two dimensional Fourier transformation.
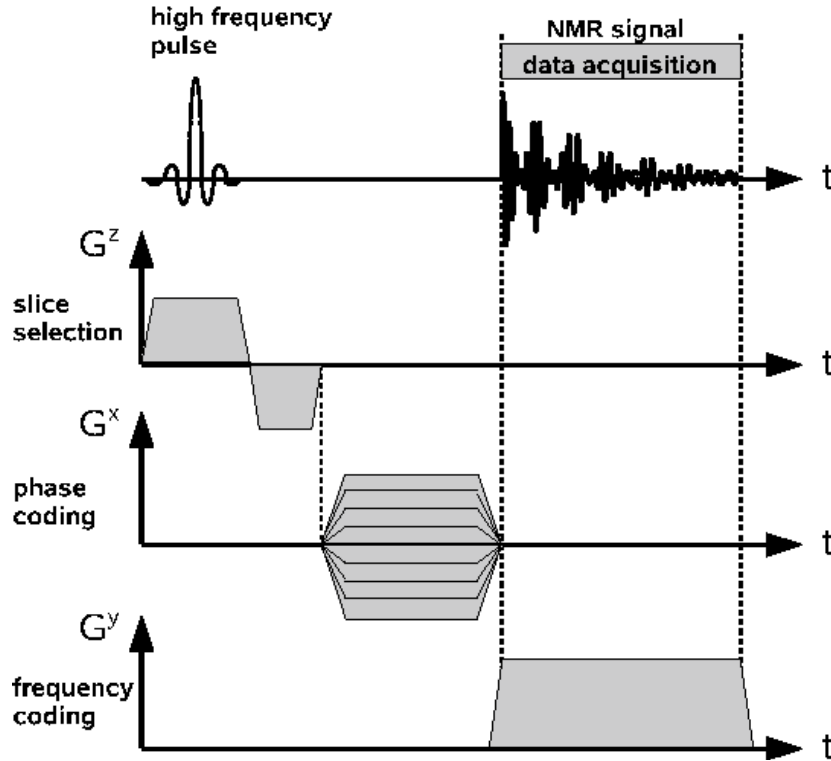
Abbildung 14: Timing diagram for the two dimensional Fourier method.

Fig. 14 shows the timing diagram of the high frequency pulse and the slice selection, the phase and frequency coding gradient for the two dimensional Fourier method. The high frequency pulse is applied while the slice selection gradient is switched on. After this pulse, the slice refocussing gradient is switched on with reversed polarity. The phase and frequency coding gradients are then switched on to record the two dimensional matrix of data points.

5.2.3   Two dimensional imaging measurements

Select the application *"msse"* for the two dimensional measurements with the Fourier method. The parameters for such a measurement are listed in a Configuration Table. The Bruker user interface lists a row of icons at the top of the graphical window. The icon for the Configuration Table is located almost in the center of this row. Left click on the icon, a graphical window *"APPLICATION CONFIGURATION TABLE"* will open. On the left, a column is listed with Imaging Options. Here, you have to define the orientation of the slice. The slice can be *"Horizontal"*, *"Vertical Back to Front"* or *"Vertical Left to Right"*. Choose the orientation by clicking on the corresponding box. On the right, the following Image Parameters are listed:

- *Field of View [mm]*: The geometrical size of the measurement. The glass tube has an outer diameter of about 24 mm, hence the measurement will show a margin of about 4 mm on each side if the *"Field of View"* is defined as 32 mm. With this choice, a measured pixel will be of dimension (0.5x0.5) mm^2. You can zoom into the center of the picture by reducing this parameter. A *"Field of View"* of 16 mm results, for example, in pixels of size (0.25x0.25) mm^2.

- *Image Size [points]*: This value defines the number of pixels in the slice and is set to 64. **Do not change this value**, the data points are measured as a 64x64 matrix by the Bruker software.

- *Slice Thickness [mm]*: The thickness of the slice. For materials with a good NMR signal like oil the minimum slice thickness is 2 mm. For materials with a weak NMR signal the minimum slice thickness is larger. If the slice thickness is defined to be too thin, then the NMR signal is too weak, and the program will not find valid data acquisition parameters.

- *Center Slice Position [mm]*: The location of the center of the slice along the gradient direction. For slices which are defined to be vertical, the center slice position zero is defined by the vertical axis of the glass tube. For a horizontal slice, the center slice position zero is defined by the height zero as shown in the one dimensional measurement made with the *"profile"* application.

- *Number of Slices*: This program can in principle record multiple slices simultaneously. The data format assumes that only one slice is recorded, hence this parameter has to be set to one.

- *Inter Slice Distance [mm]*: Only of relevance when multiple slices are recorded.

- *Echo time [ms]*: Set to 10 ms. **Do not change this value.**

- *Repetition time [s]*: Set to 0.5 s. **Do not change this value.**

- *Number of Averages*: The number of measurements over which the average is taken. Choose one measurement for checking whether the data acquisition parameters are set correctly. Choose more than one measurement if you want to have a picture with improved contrast.

Click on the *"OK"* button in the bottom left corner when all the Image Parameters are set correctly. To start the measurement, click on the blue icon *"Measure"* in the bottom left corner of the minispec interface. A graphical window *"TEXT INPUT BOX"* will now open. Here, you have to define the location and the name of the file where the data points are stored. Enter your folder name and define the name of the file such that you recognize this measurement when reading back the file for display. Click *"OK"* when done. The program optimizes the slice refocussing gradient (see Fig. 14), and then iterates through the cycles of data acquisition. The program will show *"Data exported"* when finished. You will now find two files in your folder. The file names contain some digits at the end added by the program with the information of the date and the time. Remove these digits for easier further processing of the files.

5.2.4 Two dimensional data display

A LabVIEW application *"nmr_2d.vi"* exists for displaying the data of your measurement. You can find this program by clicking on the link *"day3"* on the desktop. Enter your folder name and the file name which you want to display.

5.2.5 Two dimensional measurements

Take the following measurements with the two dimensional Fourier method:

- Take the glass tube with the 15 mm oil and define a horizontal slice. What picture do you expect? Do you see what you expect when you display your data? Repeat the measurement with a vertical slice left to right. Do you see what you expect?

- Put a peanut with shell into an empty glass tube. Choose the measurement parameters such that the two peanuts within the shell are visible. Take a peanut out of the shell. Adjust the measurement parameters such that the air gap between the two halves of the peanut is visible.

- Take a pecan nut and try to resolve the inner structure of this nut.

- Take a piece of celery and map the C-shaped form by using a horizontal slice.

6 NMR applications

NMR techniques are commonly used in many areas of basic and applied research as well as in industrial applications. A few of these applications are listed below and some links are given where further information is available.

- *Spectroscopy of ^{31}P*: Nuclear Magnetic Resonance techniques can be applied for spectroscopy of nuclei with spin not equal to zero. Of particular interest is the spectroscopy of ^{31}P due to the role of the adenosintriphosphat molecule (ATP) in the energy balance of living cells. Energy can be gained by transforming ATP into adenosindiphosphat (ADP). ATP contains three ^{31}P nuclei whereas ADP contains only two. The ^{31}P nuclei can be identified in these molecules by their chemical shift. For a particular application of ^{31}P spectroscopy see http://www.nmr.uni-duesseldorf.de/main/menergie.html

- *Magnetic Resonance Imaging*: The application of NMR techniques in medical research or for medical diagnosis is known as Magnetic Resonance Imaging (MRI). YouTube lists a multitude of video clips of MRI pictures for the diagnosis of knee injuries and brain tumors (http://www.youtube.com).

- *Biomagnetism*: The Bio Imaging Laboratory at the University of Antwerpen concentrates its research activity on high resolution in vivo MRI.
(http://webh01.ua.ac.be/biomag/)

- *Surface quality control*: Special hand held devices have been developed for measurements in the near surface volume, as is required for example in quality control for production processes of car tires.
(http://www.brukeroptics.com/profiler.html)

- *Digital fish library*: The Digital Fish Library (DFL) at the University of California San Diego gives access to the three dimensional information of many fish species which have been scanned by NMR techniques.
(http://www.digitalfishlibrary.org)

A   Appendix A: Minispec p20 Electronic Unit

The electronic unit of the minispec p20 is connected to electrical power by a portable outlet which can be switched "ON"/"OFF" manually. Switch "ON" if needed.
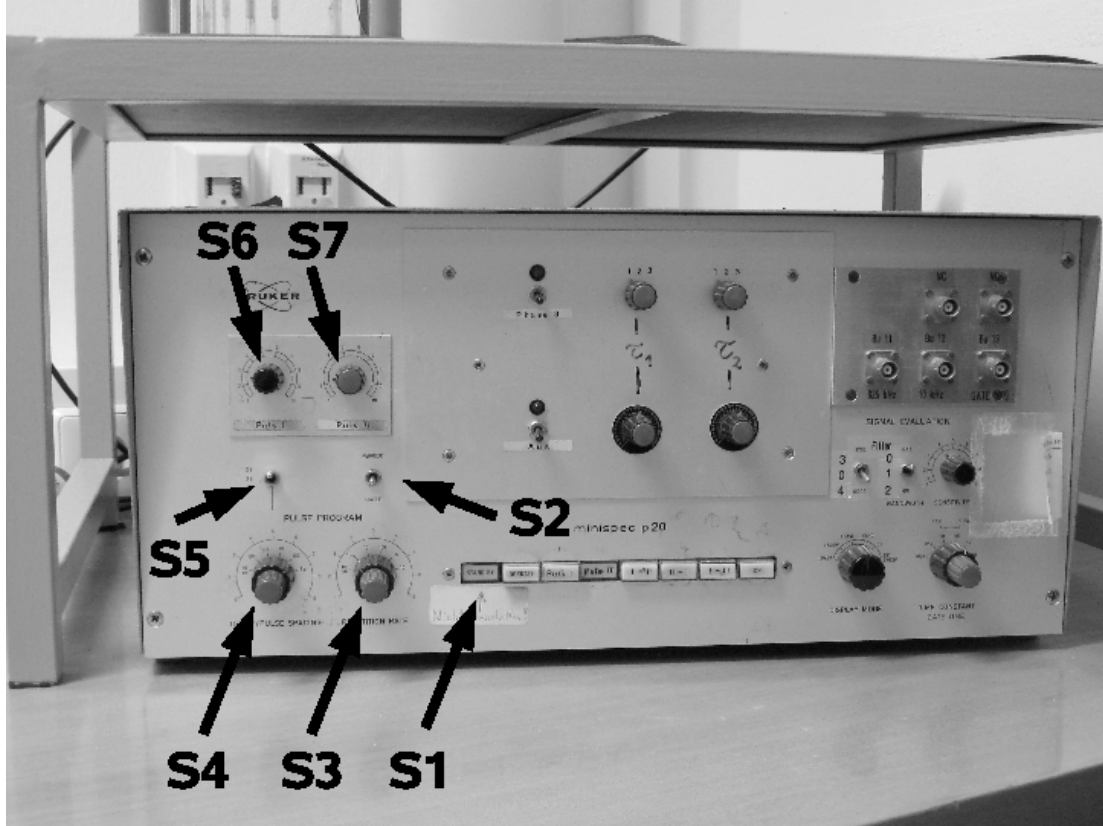

Abbildung 15: The p20 electronic unit.

The front panel of the electronic unit has different switches which have the following functions:

S1: A row of 8 push buttons for selecting the function of the minispec p20. From left to right these buttons are labeled

- **Stand by: Don't touch this button !** This button should always be in IN position.

- **OPERATE:** When pushed IN, the electronics generates pulses. To stop generating pulses, push this button into OUT position.

- **Puls I:** This button selects Puls I.

- **Puls II:** This button selects Puls II.

- **I - I:** This button selects a pulse sequence Puls I - Puls I (not used in F61/F62).

- **II - I:** This button selects a pulse sequence Puls II - Puls I.

- **I - II:** This button selects a pulse sequence Puls I - Puls II.

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- **CP:** This button selects a Carr-Purcell sequence.

S2: In *"single"* mode, this switch specifies that your selection done in S1 is generated only once. In *"periodic"* mode, your selection of S1 will be generated many times in time intervals specified by the S3 switch.

S3: This switch specifies the time interval at which your pulses are produced when S2 is in *"periodic"* mode. This switch S3 consists of an inner and outer knob. The outer knob in black is in logarithmic scale and has settings 100 μs, 1 ms, 10 ms, 100 ms, 1 s and 10 s. The inner knob in red is in linear mode and multiplies the setting defined by the black knob. Turn the red knob counterclockwise until it locks in position 1. Every click in clockwise rotation increases the multiplicative factor by one unit up to the maximum value of 9.

S4: This switch is active when a I-II, II-I or CP sequence is selected by S1. The value of S4 specifies the time interval between the two pulses of the sequence. The switch S4 consists of an inner and outer knob. The outer knob in black is in logarithmic scale and has settings 10 μs, 100 μs, 1 ms, 10 ms, 100 ms and 1 s (**Do not use the 1 s setting, it doesn't work !**). The inner knob in red is in linear mode and multiplies the setting defined by the black knob. Turn the red knob counterclockwise until it locks in position 1. Every click in clockwise rotation increases the multiplicative factor by one unit up to the maximum value of 9.

S5: The switch S5 has three positions and is a multiplicative factor to the value defined by S4. In upper position, the factor is one. In middle position, the factor is two whereas in lower position the factor is four.

S6: This knob defines the time duration of Puls I. Turn the knob counterclockwise until it is in position 1. This minimal value of S6 defines the minimum duration of Puls I. Turning the knob clockwise increases the time duration of Puls I.

S7: This knob defines the time duration of Puls II. Turn the knob counterclockwise until it is in position 1. This minimal value of S7 defines the minimum duration of Puls II. Turning the knob clockwise increases the time duration of Puls II.

B Appendix B: Minispec p20 Magnet

The minispec p20 magnet is sitting on its own table and is connected to the p20 electronics by a cable. This cable transmits the high frequency pulses generated by the electronics to the coil inside the magnet. In addition, the cable transmits the signal induced in the coil back to the electronics. The magnet is shielded by styrofoam material for minimal temperature variation when in use. Remove the top cover of the styrofoam to have a look into the magnet assembly.

The magnet consists of the following pieces:

- **M**: The two pole pieces consist of iron material. The two pieces are mounted with an air gap in between where the probes are put for the measurements.

- **B**: The iron configuration produces a magnetic field of approximately 0.5 Tesla in the air gap. This $\vec{B}$ field points from one pole shoe to the other.
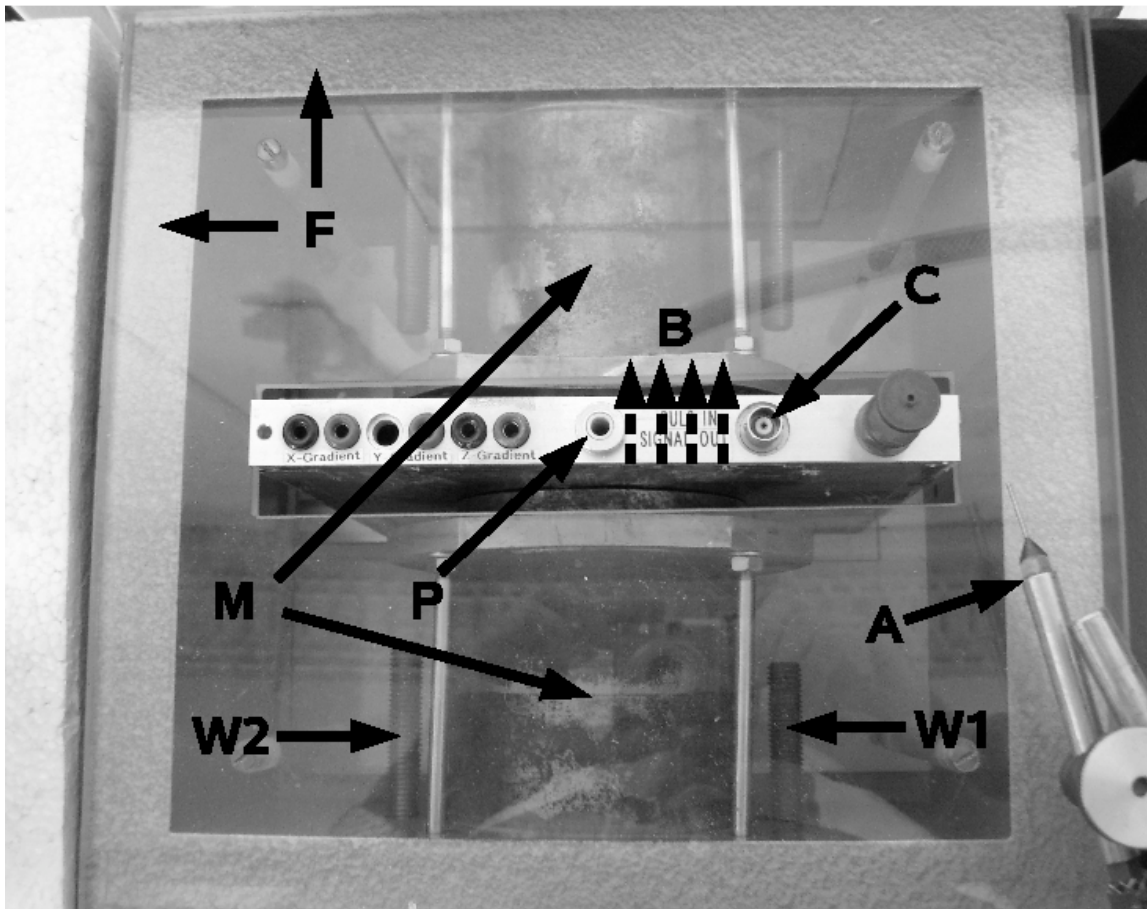
Abbildung 16: The p20 magnet.

- **F**: An iron frame holds the two pole shoes in position. This iron frame is used as return yoke for the $\vec{B}$-field lines.

- **W1,W2**: Two movable iron screws inside the frame are used to change the magnetic fringe field inside the frame. Since the moving of the screws changes the magnetic field configuration, the magnetic field in the gap can be adjusted. In particular, the screw W1 is adjustable from the outside by turning a knob. (W2 can only be changed with a screw driver, you shouldn't touch W2).

- **P**: The position P indicates where the glass tubes with the probes are positioned for the measurements.

- **C**: Connector for the cable.

- **A**: The needle for pressure air can be adjusted such that the glass tubes are put into rotation for the measurement of chemical shift. Adjust the orientation of the needle such that it points onto the small plastic ring on the tubes.

Literatur

[1] The basics of NMR are discussed in an online book by Joseph P. Hornak (http://www.cis.rit.edu/htbooks/nmr)

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[4] Fundamentals of MRI, An Interactive Learning Approach, E. Berry, A. Bulpitt, CRC Press, ISBN 978-1-58488-901-4 (a copy of this book is available at F61 for browsing)